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(54) Coated plastic caps.

(57) A cap for closing a container comprises a vapour permeable body and carries a coating of a relatively vapour impermeable material which is applied to the cap as a liquid and then cured to form a solid. The coating is permanently adhered to the cap body usually on the inside and contains a polymer which acts as a barrier usually to oxygen at least, and is preferably a vinyl chloride/vinylidene chloride copolymer or polyvinylidene chloride. Methods of making the coated caps are also disclosed.

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COATED PLASTIC CAPS

Containers such as jars and bottles for containing foodstuffs have, in the past, often been provided with metal caps of various types, such as screw caps, lug caps or crimp-on caps. Such caps are impermeable to oxygen, water vapor and other small molecules, and thus provide a good barrier between the foodstuffs and the atmosphere. This prevents ingress of oxygen and/or water vapour to protect the ingredients from becoming spoiled and egress of aromas from the foodstuffs, both of which otherwise lead to rapid deterioration of many foodstuffs. Metal caps are however being replaced by plastic caps which are cheaper, aesthetically more appealing and inert to attack from ingredients in the foodstuffs.

Plastic caps any be formed from any suitable material generally polyethylene, polypropylene, ethylene-propylene copolymer or polystyrene or mixtures of these. However these plastics are permeable to oxygen and, to some extent, water vapour. In the absence of an impermeable seal, the shelf life of the product before opening and after opening could be seriously reduced.

It is known to provide containers having plastic or metal caps with inserts comprising a laminate including an oxygen and/or water-vapour impermeable layer, such as a layer of aluminium foil. In FR 2,445,474 there are described laminar inserts for caps which have a coating of polyvinylidene chloride as a gas barrier.

In US 4379117 it is suggested that a sheet of polyvinylidene chloride is used as a insert for a crown cap i.e. a metal cap, but there is no suggestion that it could be used to render impermeable an otherwise permeable cap. The manufacture and insertion of cap inserts is expensive since they require a relatively thick layer of material and the formation and insertion of a liner is complicated. Such inserts can also be damaged during insertion and during use, e.g., opening and re-closing the container especially if the insert is, as is normal, not adhered to the cap.

To retain an insert within the cap requires either a separate provision of adhesive into the cap which requires a further processing step and has the further disadvantage that the adhesive often fails after repeated opening and closing in use, or the incorporation of protrusions on the inside of the cap to engage the insert, which can interfere with the seal between the closure and make the moulding of the cap difficult especially in the case of moulded plastic caps. In GB 2,108,892 there is described a method of compression moulding a cap having an internal lip and ribs to maintain an insert in position. The specification describes also

a method of forming the insert "in situ" by compression moulding a mass of thermoplastic material, e.g., polyvinyl chloride or ethylene vinyl acetate copolymers deposited in the inside of a cap.

5 The provision of the internal lip and ribs by the cap compression mould is complicated and the separate step of compression moulding the insert requires an additional moulding step and die. The method inevitably results in a large quantity of the insert material being used, which is expensive.

10 It is found that the seal between the top of a container and one of these known inserts is unsatisfactory and cannot provide the desired long shelf life. To remedy this defect, there has been developed a closure system having independent primary and secondary seals. The primary seal seals the container during storage and usually comprises a sheet of aluminium foil or other impermeable material stretched across the top of the container and sealed by an adhesive. The primary seal is broken when the container is first used by the consumer and cannot be reformed thereafter. The secondary seal after opening is provided by a laminated insert. The system of seals is generally provided by forming a laminate including the insert and the primary seal material, connected together by a weak adhesive, and then adhering the whole laminate to the top of the container after applying the cap. On opening the container for the first time the weak adhesive attachment between the primary seal material and the insert is ruptured. The system is complicated to manufacture and provides an unsatisfactory secondary seal, since the seal between the insert and the top of the container is very poor since, for instance, the jar often has small amount of adhesive and primary seal material adhered to it so that it is not smooth. The cap must have internal protrusions to retain the insert which have the above-described problems.

20 In DE 1,532,473 a sheet of metal foil is welded or adhered to a plastics stopper as a gas barrier. A gas impermeable sheet of rubber or plastics may replace the metal foil. The problem with such stoppers is that it is difficult to align the piece of foil or plastics sheet with the stopper in a fast automated production line, especially where a separate application of adhesive or welding step is required, and especially when the sheet is to be applied inside the stopper. When the sheet is applied to the outside of a cap it can easily become damaged during use. It is difficult or impossible satisfactorily to apply sheet material to surfaces other than flat

surfaces so that generally the top only of the outside of a stopper can be covered by a sheet, which still allows diffusion of vapours through the sheet walls.

It is also known to print information or decorative features on to the outside surfaces of caps and to coat the caps with a protective lacquer. However to our knowledge no such coatings have ever been applied to permeable caps using materials and amounts sufficient to render the caps substantially impermeable.

It would be desirable to provide a plastic cap that is capable of providing satisfactory seal properties so as to protect from the atmosphere the contents of a container closed by the cap, and that is simple and cheap to manufacture.

In the invention a cap comprises a vapour permeable body and has a coating of a vapour impermeable material which has been applied to the cap as a liquid and then cured to form a solid and which comprises a polymer and is permanently adhered to the cap. The vapour to which the uncoated cap is initially permeable, but to which it is impermeable due to the presence of the coating, may be water vapour and is preferably oxygen.

The body of the cap comprises a plastic material such as is generally used to make caps of this type. Generally the material comprises polyethylene, polypropylene, ethylene-propylene copolymers polystyrene or mixtures of these. Such materials are permeable to oxygen and/or water-vapour.

The coating may be on the inside and/or the outside of the cap. Preferably it is on the inside only of the cap, since it is less likely to be damaged during manufacture and use. It may cover the whole area of the cap, for example, the top surface and the side walls, but usually covers all or part of the top surface only. The proportion of the top surface that is covered should be sufficient to give the desired decrease in oxygen and/or water-vapour permeability. Since it is usually desirable that the permeability be as low as possible preferably the whole area of the surface is covered. If the coating is on the inside it may be desirable to leave a narrow ring around the edge of the top surface free of the impermeable material, particularly, if a gasket is to be applied in the cap.

The coating is suitably above 1 micron thick but generally needs to be no thicker than 100 microns. Preferably it is between 5 and 50 microns thick, more preferably between 5 and 15 microns thick.

The impermeable material generally comprises polymers known to be good barriers to oxygen and/or water vapour. Suitable polymers generally have halogen and/or hydroxy groups in the molecules, since these generally have good barrier

properties. Suitable polymers include polymers and copolymers of vinylidene chloride, vinyl chloride, vinyl alcohol and acrylates, and epoxy-phenolic resins, cellulose esters, polyurethanes and mixtures of these polymers. The preferred polymers are copolymers of vinyl chloride and vinylidene chloride and the most preferred polymer is polyvinylidene chloride, which gives very low permeability.

In one aspect of the invention the barrier polymer has an oxygen permeability of less than $100 - (m^2.m)/(m^2.d.PPa)$ at $23^\circ C$, 100% r.h., more preferably less than 50 and most preferably less than 20 or even less than 5. For example, polyvinylidene chloride has an oxygen permeability of 0.4 and vinylchloride polymers have oxygen permeabilities in the range 31 to 59, depending on the formulation. Vinyl chloride-vinylidene chloride copolymers have permeability between the values of the homopolymers, depending upon the relative amounts of monomers and the formulation.

In another aspect of the invention the coating is sufficient to reduce the permeability of the cap to less than 50%, preferably less than 20% and most preferably less than 10% of the caps permeability without the coating. For instance a 63mm cap of polypropylene typically has a permeability of 0.08 cc oxygen transmission per day (measured when the container sealed by the cap is filled with nitrogen and surrounded by oxygen, both at atmospheric pressure). In the invention the oxygen transmission of such a cap is preferably reduced to below 0.04, preferably below 0.01, cc O_2 per day.

Preferred caps according to the invention have bodies that are formed of polymers of propylene and/or ethylene, or other permeable polymer, have a diameter of about 10 to 100mm, usually 30-100mm a coating of a vapour impermeable material and the coated caps have a permeability of less than 0.03 cc oxygen transmission per day.

The choice of the optimum impermeable material depends on the contents of the container for which the cap is to be used. The following factors must be taken into consideration, the decrease in permeability required, whether the material is sensitive to moisture or other components of the contents, and whether the material is approved for use with foodstuffs.

For example, polyvinylalcohol is suitable for dry packs, since it has a low permeability to oxygen. Fully hydrolysed polyvinylalcohol is however water sensitive, and so for sealing containers for moisture-containing ingredients, the less sensitive, partially hydrolysed polyvinylalcohol may be used. In incompletely hydrolysed polyvinylacetate (known commercially as partially hydrolysed polyvinylalcohol) up to about 30% of the acetate groups from the original polyvinylacetate remain in the polymer.

The most preferred polymer is, as mentioned above, a homo polymer or copolymer of vinylidene chloride, for example a copolymer with vinyl chloride. These polymers are insensitive to water, highly impermeable and approved for use with food-stuffs.

The impermeable coating may comprise in addition to the barrier polymer or polymers, other components such as adhesion promoters, filler, diluent and viscosity modifiers.

According to another aspect of the invention the coating composition contains filler comprising particles having a plate-like crystal structure, for example talc, mica, flake glass and flake metal. Such fillers are impermeable and may often form an oriented structure with the crystals lying parallel to the surface of the cap, thereby increasing the length of the path along which the oxygen and/or water molecules would have to travel to permeate through the coating.

Adhesion promoters may be included in the coating since the materials from which caps are commonly made resist adhesion to most other substances. Suitable adhesion promoters are for instance oxidised or carboxylated polyolefines, such as oxidised polyethylene and other known materials.

The liquid coating composition may be applied by conventional techniques such as curtain coating, pad application, rollercoating, printing or, preferably, by spraying.

It is desirable that the coating should be substantially free of pinholes, since these would allow the passage of oxygen and/or water vapour. This problem may be reduced by, for instance, spinning the cap whilst the coating is still liquid, spreading the coating after application, or by applying a second coating over the first. A second coating is usually applied when the first coating is partially or completely dry. It may comprise a different composition. For example one layer may be particularly oxygen impermeable and the other may be particularly impermeable to water vapour but it is more convenient from a manufacturing point of view if both layers comprise the same composition.

It is generally desirable that a cap should contain a gasket to provide a good hermetic and liquid seal between the cap and the top of the container. This gasket may be of a conventional type used in plastic caps and may be provided by a process as described in our patent publication number GB 2051660B. The impermeable coating may be provided on top of the gasket, but preferably the gasket is provided over the coating, where the coating is on the inside of the cap. The coating

may in this case not extend to the edge of the cap so that an overlying gasket will be in contact with the material of the cap body as well as with the coating.

It may be desirable to provide a separate adhesive layer between the coating and the cap body to improve the adhesion. This may be formed of a known adhesion promoter, for example comprising oxidised or carboxylated polyolefine, preferably oxidised polyethylene. Alternatively, the cap material may be surface treated before application of the coating for example by oxidising the surface using a corona discharge or flaming.

In a method according to the invention the new caps are made by coating a permeable cap with a liquid composition capable of forming the impermeable barrier coating, and the liquid is cured to form a solid. Curing, in the context of this specification, includes drying, solidification of melts, gelling and chemical modification, e.g., cross linking.

The liquid composition may be water based, for example it may be a latex of a water-insoluble polymer or an aqueous solution of a water-soluble polymer. Suitable latices comprise for instance polymers and copolymers, of vinylidene chloride or acrylate polymers such as methylmethacrylate polymers. The composition may comprise viscosity modifying agents, generally thickening agents for example in amount in the range 0 to 5% based on the solids content of the latex. A suitable thickening agent for a polyvinylidene chloride latex which is acidic is polyvinylpyrrolidone. Methylmethacrylate latices generally have an alkaline pH and suitable thickening agents stable in such conditions, include most water soluble thickening agents such as natural polymers or their derivatives, e.g., alginates, and synthetic polymers such as water soluble acrylates. The liquid composition has a total solids content in the range 20 to 80%, preferably 40 to 60%, of which 50 to 100% is polymer and up to 50% is filler.

Completely or partially hydrolysed polyvinylacetate may be applied as an aqueous solution which may also comprise adhesion promoters, fillers and viscosity modifiers. The solution generally has a polymer content 50 to 100% is polymer and up to 50% is filler. The polymer may suitably be cross linked after application to improve its physical properties, for example during drying of the coating, for example with conventional cross linking reagents. Especially for use with foodstuffs, the cross-linking reagent is selected from low toxicity agents such as amino resins. Polyvinylalcohol coatings are most suitable for dry packs since their permeability increases on exposure to moisture.

Aqueous-based compositions are often preferred to solvent-based compositions since the latter may be hazardous to health during manufacture and use and to the environment and the solvent must be recovered in the manufacturing process which is expensive.

Solvent based compositions may be preferred in some circumstances, for example where rapid drying is necessary. Example are solutions of copolymers of vinyl chloride with vinylidene chloride, for example in ketonic solvents in which they are stable. Such solutions generally have a rather low solids content, for example 5 to about 25%, usually about 15% by weight. The solutions may contain fillers, adhesion promoters and viscosity-modifiers. Other solvent based compositions are for example epoxy phenolic lacquers and solutions of organic or inorganic esters of cellulose, these solutions optionally containing other components. The solvent based compositions may be allowed to dry at about room temperature or may be heated to accelerate the rate of drying. Heating may also cure the polymers, for example by cross linking the polymers by conventional mechanisms. Cross linking improves the properties, especially the mechanical properties, of epoxy phenolic resins.

The liquid coating compositions may also be provided as hot melt compositions. These are suitable for high molecular weight polymers which are insoluble and which are not degraded by heat. Generally the polymer should have a melting temperature lower than that of the cap material, so that the melt can be applied at a temperature which will not distort the cap. The cap may be heated prior to application of the coating to improve the adhesion of the coating to the cap. In some instances it may be desirable to apply the coating at a temperature greater than that of the melting point of the material of the cap so that the surface of the cap is melted by the coating material which will give even more improved adhesion of the coating to the cap in which case polymers having a melting point greater than that of the material of the cap could be used in the formulation of the coating. In a carefully controlled process this surface melting can be achieved without distorting the cap. The hot melt polymer is suitably an ethylene-vinylalcohol copolymer. The hot melt composition may comprise an adhesion promoter, such as oxidised or carboxylated polyolefin, and generally a viscosity-modifier, which is usually a viscosity-reducing diluent for example in an amount of 5 to 30% by weight. Diluents which are compatible with hot melt ethylene-vinyl alcohol copolymer compositions are for instance polyethylene wax, oxidised or carboxylated polyethylene wax, polyamide resins, polyterpene resins and esters of rosin, hydrogenated rosin or disproportionated rosin. The compositions may

contain filler in an amount of 5 to 50%. They are generally applied at a temperature in the range 80 to 200°C, preferably 100 -160°C. Hot melt compositions have the advantage that the caps do not have to be passed through an oven after the coating step which saves time and energy.

Other systems which may be suitable for use are curable liquid polymer compositions. Although some of the compositions may not yet be approved for use with food, they are useful for coating the external surface of a cap or the internal surfaces of caps not used with foodstuffs. The compositions are generally curable by exposure to radiation, often UV light or electron beam radiation. The compositions thus comprise initiators, acceptors and other catalysts for the curing system. Many curable compositions are known and may for instance comprise monomers or oligomers of urethanes, epoxy resins, unsaturated esters, acrylates etc. The compositions suitably comprise adhesion promoters as listed above.

In the process the cap may be provided with a gasket, for example a flowed-in gasket of the type disclosed in GB2051660B. This gasket may be applied before the coating but is preferably applied after the coating. In the latter process the thermal and micro wave energy used to flux the gasket composition is effective to cure the coating composition, for example to volatilise the solvent or to cross link the polymer molecules.

The surface of the cap body to be coated may be pretreated in the process to improve the adhesion of the coating. For example the surface of a polyolefine body may be surface treated to oxidise some of the polyolefine molecules. Such treatment may be by corona discharge or flaming.

The new caps are generally screw caps and are of particular use for closing otherwise impermeable containers such as glass jars and bottles. They may also be useful in closing plastic containers, for example formed of polyolefines or polyesters, optionally themselves coated with a water-vapour and/or oxygen impermeable coating. The containers are useful in packaging many types of products, for example pharmaceuticals and, especially, foodstuffs. The cap may be provided with conventional tamper-evident seals. As well as preventing ingress of oxygen and water-vapour and thereby protecting the contents of a container from deterioration, the plastic caps are generally also impermeable to aroma chemical and carbon dioxide and thus may prevent egress of such chemicals so that the content may retain their taste and carbonation for longer than in containers closed by uncoated caps.

The following examples illustrate the invention.

Example 1

A latex polyvinylidene chloride, solids concentration 50% by weight, sold under the trade name Daran 820 by W R Grace & Co. was used to coat a cap. The specific permeability of Daran is quoted as 2.5 ml oxygen per 100 in² film 1 micron thick per 24 hours at 1 bar pressure difference, measured at 25°C and 65% r.h. (0.39 (m².m)/(m².day.PPa)). The emulsion has a maximum value for the Brookfield (LVF) viscosity of 30cP (No.1 spindle at 60vpm, 25°C). The emulsion was sprayed onto the internal surface of a 63mm diameter polypropylene cap which had previously been washed and dried, so as to give a dry film thickness of approximately 20 microns. An infra-red lamp and hot air circulating at 115-120°C were used to dry the film of wet compound.

Example 2

Into the latex used in example 1 was stirred 300 mesh micronised mica at a concentration of 15 parts by weight per 100 parts of polymer solids, so as to give a smooth dispersion. The composition was applied as in example 1 at a similar rate.

Example 3

A copolymer of vinyl chloride and vinylidene chloride (exam SGA/1 -Solvay et cie) having a specific oxygen permeability of 2×10^{-11} ml per m² film 1 micron thick per day per atmosphere pressure difference measured at 23°C and 85% r.h. (20(m².m)/(m².day.PPa)) was dissolved in methylethyl ketone to give a 15 weight % solution. The solution was applied to a cap as in example 1.

Example 4

As ethylene-vinyl alcohol copolymer, formed from about 80% molar ethylene, and having vicat softening point of 76°C and melting point - (measured by differential thermal analysis) of 93°C having a specific oxygen permeability of 5×10^{-11} ml per cm² film 1cm thick per second per cm Hg pressure difference measured at 37°C, 0% r.h. (324(m².m)/(m².day.PPa)), sold under the trade name Dumilan D219 (Takeda Chemical Industries Ltd.), was applied as a hot melt composition by the same method as example 1.

Claims

1. A cap comprising a vapour permeable body carrying a coating of a relatively vapour impermeable material which has been applied to the cap as a liquid and then cured to form a solid and which comprises a polymer and is permanently adhered to the cap.

2. A cap according to claim 1 in which the vapour includes oxygen.

3. A cap according to claim 1 or claim 2 in which the coating reduces the vapour permeability of the cap to less than 50%, preferably to less than 20% and more preferably to less than 10% of its uncoated permeability.

4. A cap according to any preceding claim in which the polymer of the coating has an oxygen permeability of less than 100(m².m)/m².d.P.Pa at 23% and 100% r.h., preferably less than 50, more preferably less than 20.

5. A cap according to any preceding claim in which the cap body comprises polyolefine, preferably one or more polymers selected from polyethylene, polypropylene, ethylene-propylene copolymers and polystyrene.

6. A cap according to any preceding claim in which the coating is on the inside of the cap.

7. A cap according to any preceding claim in which the coating polymer is selected from polymers and copolymers of vinylidene chloride, vinyl chloride, vinyl alcohol and acrylates, epoxy-phenolic resins, cellulose esters, polyurethanes and mixtures thereof, preferably a polymer or copolymer of vinylidene chloride.

8. A cap according to any preceding claim in which the coating comprises filler having a plate-like crystal structure, preferably selected from talc, mica, flake glass and flake metal.

9. A cap according to any preceding claim comprising an adhesive layer between the coating and the cap comprising an adhesion promoter, preferably selected from oxidised and carboxylated polyolefines, most preferably oxidised polyethylene.

10. A method of making a cap according to any preceding claim in which a vapour permeable material is coated with a liquid composition containing a relatively vapour-impermeable polymer and the liquid is cured to form a solid.

11. A method according to claim 10 in which the composition is a latex of a water-insoluble polymer, preferably selected from polymers and copolymers of vinylidene-chloride and acrylate polymers.

12. A method according to claim 10 in which the polymer is applied as an aqueous solution of a water-soluble polymer, preferably comprising polyvinylalcohol.

13. A method according to claim 10 in which the polymer is applied to the cap as a hot melt composition, the polymer preferably comprising ethylene-vinylalcohol copolymer.

14. A method according to any claims 10 to 13 in which the cap material is surface treated before application of the coating, preferably by oxidising the surface using a corona discharge or by flaming..

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D, Y	FR-A-2 514 326 (H.C. INDUSTRIES) * Page 4, lines 11-21; figure 1 *	1, 10	B 65 D 41/00
A		4, 5	
Y	GB-A-2 071 522 (DAIMLER-BENZ AG) * Page 1, lines 79-96; claim 1 *	1, 10	
A		5, 7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			B 05 D B 32 B B 65 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15-04-1987	Examiner VAN THIELEN J.B.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	